Title of the Invention:

ORGANIC EL DEVICE AND PRODUCTION METHOD THEREOF

Technical Field:

This invention relates to an organic EL (electro-luminescence) device as an electric light emitting device for use in a display, a display light source, etc, and to a production method thereof.

Background Art:

Recently, development of an organic EL display device using organic materials has been accelerated as a spontaneous light emitting display that will replace liquid crystal displays. Organic EL devices using the organic materials are principally described in the reference "Appl. Phys. Lett." 51(12), 21 September, 1987, p913, that teaches a vacuum deposition method of organic materials having a low molecular weight, and in the reference "Appl. Phys. Lett." 71(1), 7 July, 1997, p.34 et seq. that teaches an application method of organic materials having a high molecular weight.

As means for achieving color display in the case of the low molecular weight materials, a method that vacuum deposits different light emitting materials onto desired pixels through a mask has been employed. As to the high molecular weight materials, on the other hand, a coloring method using an ink jet method has drawn an attention because it can execute patterning delicately and easily. Examples of the formation of organic EL devices by the ink jet method are known from Japanese Patent Laid-Open Nos. 235378/1995, 12377/1998, 153967/1998, 40358/1999, 54270/1999 and 339957/1999.

From the aspect of a device structure, a hole injection/transportation layer is formed in many cases between an anode and a light emitting layer to

improve light emission efficiency and durability ("Appl. Phys. Lett." 51, 21 September, 1987, p913). Incidentally, the term "hole injection/transportation layer" used herein is a generic term of a layer that has a function of injecting and transporting holes from the anode side to a light emitting layer. According to the prior art technology, a film of a buffer layer or a hole injection/transportation layer is formed by using conductive polymers such as polythiophene derivatives or polyaniline derivatives by an application method such as spin coating ("Nature", 357, 477, 1992). A report has been made to the effect that the hole injection/transportation layer is formed by vacuum depositing phenylamine derivatives as the low molecular weight material.

An ink jet system is extremely effective as means for easily forming a film having a miniature pattern without wasting organic thin film materials.

However, when an organic EL device having a laminate structure is formed in accordance with the ink jet system and moreover, when the laminate structure consists of a hole/injection layer plus a light emitting layer, for example, an underlying layer as the conductive layer is exposed when a cathode is formed if an application region of the hole injection/transportation layer as the underlying layer is broader than the application region of the light emitting layer as an upper layer with the result that a current leaks and the resulting device has low efficiency.

Disclosure of the Invention:

In a production of an organic EL device having a laminate structure by an ink jet method, it is therefore an object of the present invention to provide a high efficiency organic EL device free from a current leak and a production method thereof.

According to the present invention, there is

provided (1) an organic EL device having a structure in which a laminated film of at least two layers is formed by an ink jet system and which includes a hole injection/transportation layer and a light emitting layer, a film formation region of the light emitting layer being equal to, or greater than, a film formation region of the hole injection/transportation layer.

According to the present invention, there is also provided a method of producing an organic EL device having a structure in which a laminated film of at least two layers is formed by an ink jet system and which includes a hole injection/transportation layer and a light emitting layer, characterized in that, when a discharge amount of an ink composition for forming the hole injection/transportation layer is A and a discharge amount of an ink composition for forming the light emitting layer is B, a relation $A \leq B$ is satisfied.

According to the present invention, there is further provided a method of producing an organic EL device having a structure in which a laminated film of at least two layers is formed by an ink jet system and which includes a hole injection/transportation layer and a light emitting layer, characterized in that, when a sum of discharge amounts of an ink composition for forming the hole injection/transportation layer is A and a sum of discharge amounts of an ink composition for forming the light emitting layer is B, a relation $A \leq B$ is satisfied.

Brief Description of Drawings:

Fig. 1 is a sectional view showing a step of a production method of an organic EL device according to one embodiment of the present invention.

Fig. 2 is a sectional view showing another step of the production method of the organic EL device according to one embodiment of the present invention.

Fig. 3 is a sectional view showing another step of the production method

of the organic EL device according to one embodiment of the present invention.

Fig. 4 is a sectional view showing still another step of the production method of the organic EL device according to one embodiment of the present invention.

Fig. 5 is a sectional view showing still another step of the production method of the organic EL device according to one embodiment of the present invention.

Fig. 6 is a sectional view showing still another step of the production method of the organic EL device according to one embodiment of the present invention.

Fig. 7 is a sectional view showing a structural example of an organic EL device.

Fig. 8 is a sectional view showing a substrate structure used in one embodiment according to the present invention.

Fig. 9 is a graph for comparing a voltage-light emission efficiency characteristic of an organic EL device according to an embodiment of the present invention.

Fig. 10 is a graph for comparing a voltage-current characteristic of an organic EL device according to an embodiment of the present invention.

Best Mode for Carrying Out the Invention:

In an organic EL device having a structure in which at least two laminated films are formed by an ink jet system and which contains a hole injection/transportation layer and a light emitting layer, the present invention has a feature in that a film formation region of the light emitting layer is equal to, or greater than, a film formation region of the hole injection/transportation layer.

In the present specification, the term "film formation region of light emitting layer is equal to, or greater than, film formation region of hole injection/transportation layer" means, for example, that the film formation area or volume of the light emitting layer as viewed plane-wise is equal to, or greater than, the film formation area or volume of the hole injection/transportation layer as viewed plane-wise.

The structure described above can prevent the leak between the hole injection/transportation layer and the cathode and can accomplish an organic EL device having high efficiency.

In a production method of an organic EL device having a structure in which at least two layers of laminated films are formed by an ink jet system and which includes a hole injection/transportation layer and a light emitting layer, the present invention has another feature in that when a discharge amount of an ink composition for forming the hole injection/transportation layer is A and a discharge amount of an ink composition for forming the light emitting layer is B, a relation $A \leq B$ is satisfied.

According to such a production method of an organic EL device, the relation $A \leq B$ is characterizingly satisfied between the discharge amount A of the ink composition for forming the hole injection/transportation layer and the discharge amount B of the ink composition when the light emitting layer is formed. When this condition is satisfied, the film formation region of the light emitting layer can be made equal to, or greater than, the film formation region of the hole injection/transportation layer. Accordingly, an organic EL device having high efficiency and free from the leak can be produced when producing an organic EL device having a laminate structure and produced by an ink jet system.

In a production method of an organic EL device having a structure in which at least two layers of laminated films are formed by an ink jet system

and which contains a hole injection/transportation layer and a light emitting layer, the present invention has another feature in that when the sum of discharge amounts of an ink composition for forming the hole injection/transportation layer is A and the sum of discharge amounts of an ink composition for forming the light emitting layer is B, the relation A ≤ B is satisfied.

According to such a production method of an organic EL device, the relation A ≤ B is characterizingly satisfied when the sum of the discharge amounts of the ink composition for forming the hole injection/transportation layer is A and the sum of the discharge amounts of the ink composition for forming the light emitting layer is B. When this condition is satisfied, it is possible to improve patterning accuracy, to set the film formation region of the light emitting layer to be equal to, or greater than, the film formation region of the hole injection/transportation layer, and to produce an organic EL device having high efficiency and free from the leak. Since patterning accuracy is high, light emission with higher uniformity can be acquired in a panel, or the like, having a large number of pixels.

Hereinafter, an embodiment of the present invention will be concretely explained with reference to the drawings.

The production method of an organic EL device by the ink jet system is the method that comprises the steps of preparing respective ink compositions by dissolving or dispersing materials of hole/injection transportation layer made of organic materials for forming the device and light emitting materials in a solvent, discharging the ink composition from an ink jet head to form a pattern on a transparent substrate, and forming the hole injection/transportation layer and the light emitting material layer.

Fig. 1 shows a sectional view of a substrate used for producing an organic EL device by the ink jet system. ITO 11 is patterned as transparent pixel

electrodes on a glass substrate 10 or a substrate equipped with TFT. Partitions (hereinafter called "banks") 13 consisting of SiO_2 12 and an organic ink-repellent material or an organic material rendered ink-repellent are disposed in regions that partition the pixels. The shape of those banks, that is, the open shape of the pixels, may be any of a circle, an ellipse, a rectangle or a stripe. Since the ink composition has a surface tension, the corners of the rectangle are preferably rounded.

Figs. 2 to 6 are drawings that illustrate a laminate layer of a hole injection/transportation layer + light emitting layer and a device production process by the ink jet system. An ink composition 14 containing a hole injection/transportation material is discharged from an ink jet head 15 and is applied into a pattern. After the ink composition is applied, the hole injection/transportation layer 16 is formed by removing the solvent and/or conducting heat treatment or causing a nitrogen gas to flow.

Subsequently, an ink composition 17 containing the light emitting materials is applied onto the hole injection/transportation layer, and the light emitting layer 18 is formed by removing the solvent and/or conducting heat treatment or causing a nitrogen gas to flow.

Thereafter, a cathode 19 is formed by vacuum deposition or sputtering of a metal such as Ca, Mg, Ag, Al, Li. To protect the device, a seal layer 20 is further formed from an epoxy resin, an acrylic resin or liquid glass, and the device is completed. An electrode made of a reflective metal material is used as an anode in place of the transparent electrode 11. A layer of a co-evaporation material such as Ag or Mg is disposed as the cathode. Thus, an organic EL device of the type from which light outgoes through the cathode side can be acquired.

Figs. 6 and 7 show the sectional structure of the resulting device.

In the device structure shown in Fig. 7, the hole injection/transportation layer 21 and the cathode 23 keep contact with each other, and current leak develops and lowers device characteristics. To prevent the current leak, it is necessary for the structure of the organic EL device that the film formation region of the light emitting layer 18 be equal to, or greater than, the film formation region of the hole injection/transportation layer 16 as shown in Fig. 6. When an electron injection/transportation layer is further to be laminated, the current leak does not occur even when the film formation region of the light emitting layer is smaller than film formation region of the hole injection/transportation layer provided that the film formation region of the electron injection/transportation layer is equal to, or greater than, the film formation region of the hole injection/transportation layer. However, a drawback occurs in that the light emitting region becomes narrower.

To form a laminated film free from the current leak, it is necessary to satisfy the relation $A \le B$ with A representing the discharge amount of the ink composition for the hole injection/transportation layer and B representing the discharge amount of the ink composition for the light emitting layer when the application of the ink composition is made once per pixel (by one droplet). When the amounts of A and B are reduced and the ink compositions are consecutively applied a large number of n and m times per pixel, respectively, the sums of the discharge amounts must satisfy the relation $nA \le mB$. These A and B amounts may well be adjusted suitably in accordance with the size of the pixels and the specification of the ink jet head (nozzle diameter, etc) used.

Incidentally, the present invention can be applied to organic EL devices of both active matrix system and passive matrix system.

The present invention will be explained in further detail with reference to the following examples but is not particularly limited thereto.

(Example 1)

Fig. 8 shows a substrate used in this example. Though the drawing shows only one pixel, these pixels were arranged in a 70.5 µm pitch. A bank was formed from a laminate layer of polyimide 27 and SiO_2 28 by photolithography on a glass substrate 26 on which ITO 25 was patterned. A bank diameter (open diameter of SiO_2) was 28 µm and a height was 2 µm. Opening at the uppermost part of the polyimide bank was 32 µm. Before an ink composition of a hole injection/transportation material was applied, the polyimide bank 28 was subjected to ink-repelling treatment by atmospheric plasma treatment. The condition of the atmospheric plasma treatment was at an atmospheric pressure and power of 300 W with a distance between an electrode and the substrate being 1 mm. In oxygen plasma treatment, an oxygen gas flow rate was 80 ccm, a helium gas flow rate was 10 SLM and a table conveying speed was 10 mm/sec. In subsequent plasma CF_4 processing, a CF_4 gas flow rate was 100 ccm, a helium gas flow rate was 10 SLM and a table conveying speed was 5 mm/sec. A composition shown in Table 1 was prepared as an ink composition for a hole injection/transportation layer.

Table 1:

Ink composition for hole injection layer

composition	material name	content (wt%)
hole injection/ transportation material	PEDT/PSS ("Bytron P") (aqueous dispersion)	7.25
polar solvent	water	52.75
	methanol	5
	isopropyl alcohol	5
	1,3-dimethyl-2-imidazolidinone	30

silane coupling agent	γ-glycidyloxypropyltrimethoxysilane	0.08

After the surface treatment of the substrate, 15 pl of the ink composition for the hole injection/transportation layer, tabulated in Table 1, was discharged and applied into a pattern from a head (model MJ-930C of Epson Co.) of an ink jet printing apparatus. The solvent was removed at 1 Torr and a room temperature for 20 minutes, and heat treatment was then conducted in the open air at 200°C (on a hot plate) for 10 minutes to form the hole injection/transportation.

A composition tabulated in Table 2 was prepared as an ink composition for the light emitting layer.

Table 2:

Ink composition for light emitting layer (green)

composition	material name	content (wt%)
light emitting material	PPV precursor solution (1.5 wt%) (water/methanol = 5/95 mixture solution)	20
polar solvent	1,3-dimethyl-2-imidazolidinone	70
	butylcarbitol acetate	10

First, 20 pl of the ink composition for the light emitting layer, tabulated in Table 2, was discharged and applied into a pattern from a head (model MJ-930C of Epson Co.) of an ink jet printing apparatus. After the solvent was removed at 1 Torr and a room temperature for 20 minutes, heat treatment was conducted at 150°C for 4 hours in a nitrogen atmosphere to conjugate the composition and to form a green light emitting layer.

Ca and Al were sputtered to thickness of 20 nm and 200 nm, respectively,

to form a cathode, and sealing was finally conducted by using an epoxy resin. The device fabricated by this example was called "device (1)".

A color device and a color panel could be fabricated by dividedly forming different pixels by using ink compositions containing light emitting materials having different light emission colors, such as green, red and blue.

(Example 2)

A device was fabricated in the same way as in Example 1 with only the exception that the discharge amounts of the ink composition for the hole injection/transportation layer and the ink composition for the light emitting layer were changed. The discharge amounts were 15 pl for the ink composition for the hole injection/transportation layer and 15 pl for the ink composition for the light emitting layer, too. The device fabricated by this Example was called "device (2)".

(Example 3)

A device was fabricated in the same way as in Example 1 with only the exception that the discharge amounts of the ink composition for the hole injection/transportation layer and the ink composition for the light emitting layer and the number of times of their discharging were changed.

The ink composition for the hole injection/transportation layer in an amount of 5 pl was continuously discharged three times to the same pixel while the ink composition for the light emitting layer (Table 1) in an amount of 10 pl was continuously discharged two times to the same pixel. When each composition was discharged several times by reducing its discharge amount, the diameter of the droplet became smaller. Because the droplets that had already been discharged and stored inside the pixel pulled subsequent droplets, accuracy of the impact point could be improved. The device fabricated in this embodiment was called "device (3)".

(Example 4)

A composition tabulated in Table 3 was prepared as the ink composition for the light emitting layer.

Table 3:

Ink composition for light emitting layer (green)

composition	material name	content (wt%)
light emitting material	PPV precursor solution (1.5 wt%) (water/methanol = 5/95 mixture solution)	30
polar solvent	1,3-dimethyl-2-imidazolidinone	60
	butylcarbitol acetate	10

The ink composition for the hole injection/transportation layer was the same as used in Examples described above (Table 1). Next, 20 pl of the ink composition for the hole injection/transportation layer and 10 pl of the ink composition for the light emitting layer were discharged. The other conditions were the same as those of Example 1. The device fabricated in this example was called "device (4)".

Figs. 9 and 10 show current-voltage characteristics and efficiency-voltage characteristics of the devices (1) and (4) fabricated in Examples 1 and 4, respectively. In the device (4), a current leak was observed in a low voltage region below a threshold voltage (Vth). For this reason, a curve of light emission efficiency rose more smoothly than in other devices not having the leak, and efficiency was lower, too. In the devices (1) to (3), high efficiency devices free from the current leak could be obtained.

When a substrate having 200 x 200 pixels was formed under the same condition

as that of Example 3, a green light emitting device that was uniform throughout the entire surface could be obtained.

(Example 5)

Next, an example using materials that were soluble in an organic solvent was represented as the ink composition for the light emitting layer. Though this example used polydioctyl fluorine as a blue color light emitting layer, the present invention is not limited to polydialkyl fluorenes but can also use polydialkylfluorene derivatives and polyparaphenylene vinylene derivatives.

A composition as an ink composition for a light emitting layer tabulated in Table 4 and a composition as an ink composition for a hole injection/transportation layer tabulated in Table 5 were respectively prepared.

Table 4:

Ink composition for hole injection layer

composition	material name	content (wt%)
hole injection/ transportation material	PEDT/PSS ("Pytron P") (aqueous dispersion)	7.25
	PSS (polystyrenesulfonic acid)	0.94
polar solvent	water	51.81
	methanol	5
	isopropyl alcohol	5
	1,3-dimethyl-2-imidazolidinone	30

Table 5:

Ink composition for light emitting layer (blue)

composition	material name	content
light emitting material	polydioctyl fluorine	1 g
non-polar solvent	cyclohexylbenzene	100 ml

After the plasma treatment was conducted in the same way as in Example 1, 15 pl of the ink composition for the hole injection/transportation layer (Table 4) was discharged and applied into a pattern. The solvent was removed in vacuum (1 Torr) and at room temperature for 20 minutes. Heat treatment was then conducted in open air at 200°C (on a hot plate) for 10 minutes, thereby forming the hole injection/transportation layer.

Next, 20 pl of the ink composition for the light emitting layer (Table 5) was discharged and applied into a pattern, and the solvent was removed in vacuum (1 Torr) and at room temperature for 20 minutes. Heat treatment was then conducted in a N_2 atmosphere at 50°C for 20 minutes, thereby forming the light emitting layer. As a cathode, Ca was vacuum evaporated to a thickness of 20 nm and Al was sputtered to 200 nm. Finally, sealing was conducted by using an epoxy resin. This device, too, provided a high efficiency device free from the current leak in the same way as the device of Example 1. In the device fabricated by using the same ink compositions and discharging 20 pl of the ink composition for the hole injection/transportation layer and 10 pl of the ink composition for the ink composition, the current leak was observed even below a threshold voltage, and its light emission efficiency was lower than that of the device described above.

As described above, when fabricating an organic EL device having a laminate structure by an ink jet system, the present invention sets a discharge amount of an ink composition for a light emitting layer to be greater than a discharge amount of an ink composition for a hole injection/transportation layer. In

this way, the present invention can make a film formation region of the light emitting layer greater than the film formation region of the hole injection/transportation layer, and can provide an excellent organic EL device free from a current leak and having high light emission efficiency.